

Interactive comment on “Atmospheric black carbon can exhibit enhanced light absorption at high relative humidity” by Y. Wei et al.

Anonymous Referee #1

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The authors report on measurements of light absorption determined from the difference method (extinction minus scattering) made in Houston, TX as a function of relative humidity. They purport to observe a substantial increase in absorption at high RH relative to low RH. Their conclusions hinge on accurate truncation correction of their scattering data, as small errors in scattering can lead to large errors in the derived absorption. After reading through the manuscript carefully, I am not convinced that the truncation correction, as applied here, has sufficient accuracy to support the conclusions. Given that direct absorption measurements, such as photoacoustic spectroscopy, remain unable to measure absorption accurately at elevated RH (Langridge et al., 2013), there is certainly a need to try and assess the influence of water uptake on light absorption using alternative methods, such as the difference method used here. However, I am

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not convinced by the data presented here that the substantial enhancement observed is real, and not just an artefact of the measurements. It is always possible that the measurements are correct, and to some extent they probably are; if correct they have great importance. Unfortunately, I have not been convinced that the measurements are sufficiently robust, and must recommend rejection. To quote from the authors: “setting specific quantitative bounds on the enhancement factor remains challenging.”

Major Concern:

Shouldn't the correction for truncation be size dependent? According to Qian (2012) it is. This does not seem to be accounted for robustly in the truncation correction as applied in this study. The authors have accounted for size to some extent in that their truncation correction factor increases with RH, to indicate an increase in particle size with water uptake. But this does not account for variations that might occur in the dry particle size and seems to a priori assume a size for the dry particle distribution. This is relevant because no size cut was applied (P29416, L23), and thus the contributions of supermicron particles may be variable, especially given the proximity of the sampling site to the ocean. This could lead to biases in the truncation correction, as applied here, that depend on the sampled air mass. In more “aged” air masses in Houston, this often corresponds to air that has been recirculated and is returned from over the ocean. In fact, the authors note that back trajectory analysis indicates many of the air masses “originated from over the Gulf of Mexico” (P29423, L13). Thus, one might think that the contributions of supermicron particles could be larger for the “aged” air masses, when the largest MAC values are observed. I have not been convinced that the truncation correction has been applied in a systematic way that accounts for variations in the sampled particle size distribution, and thus I am not convinced that there are not important sampling biases associated with the measurement of absorption via the difference method in this study, especially at elevated relative humidities. Based on Qian et al. (2012), a correction factor of 1.05 corresponds to a particle size of 500 nm. Based on what is shown in Fig. 2, a correction factor of 1.05 corresponds to ~85%

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RH. Thus, this would imply that the assumed mean (optically weighted) size of the particles at 85% RH is only 500 nm. Given a growth factor of ~ 1.6 at 85% RH (from Fig. 2a), this corresponds to a mean (optically-weighted) size of only 312.5 nm. The use of such a size implies minimal contribution from supermicron particles (or larger particles in general) to the scattering. The correction for particles that are 1000 nm is 1.12 (Qian et al.). Given the mean reported values for extinction and scattering in Table 1, if the appropriate correction factor were 1.12 instead of 1.05, this would correspond to a substantial decrease in the calculated absorption: from 2.9 Mm⁻¹ to 1.17 Mm⁻¹, or a decrease by 60%. Further, the calculations in Qian et al. (2012) indicate that the correction factor increases as the refractive index decreases, which it will when water is taken up onto particles. It is not clear whether this has been accounted for, but I do not believe that it has. Also, the observed correction factors in Qian et al. (2012) are substantially smaller than theoretical calculations and it is postulated that one reason is due to “perhaps non-sphericity of the salt particles” used in testing. As particles take up water, it is reasonable to assume that the particles would become more spherical, so it may be that the observations in Qian et al. underestimate the correction factor for ambient humidified particles. Clearly, appropriate accounting of the truncation correction is critical to this entire analysis, and the above numerical example is simply meant to serve as an example of this importance. I have not been convinced that an appropriate, rigorous accounting of size-dependent, RI dependent and (potentially) shape dependent variations in the truncation correction has been performed in this study. The RH-dependent correction factor is not a constant, as Fig. 2b would imply, but depends explicitly on current conditions. No size distributions are available (at least not presented) that would allow them to assess how variations in the size of non-BC containing particles, which will likely dominate the scattering, could have affected the results. The authors simply postulate a correction factor as a function of RH (Fig. 2b) without sufficient details as to how this was derived. I have difficulty thinking that their scheme could account for all of the variability and complications associated with determining an accurate value of the correction factor for use at each point in time in their

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observations. Unfortunately, the entire study hinges on the accuracy of the truncation correction. For this reason (and others elaborated upon below) I must suggest rejection of this work.

Other concerns/comments:

Particles were not size size cut during sampling, and given the near ocean environment one might expect some fraction of presumably hygroscopic supermicron particles. Such particles are lost in inlets and transfer lines more easily than are smaller particles. This is especially true as the particles take up water and grow to larger sizes (although the low density of water has some compensating effect). How can the authors know that the particle losses in the ambient/humidified line and the dried line are identical, especially since particles are sampled through a tee? If losses are greater in the ambient/humidified channel, and if these losses are biased towards larger particles that are likely to be less absorbing than the smaller particles, then the scattering in this channel will be underestimated, as will be the extinction. Since absorption here is determined as the difference between extinction and scattering, it is likely that such losses would lead to overestimates of absorption in the humidified channel. Particle losses are not discussed. This presents a major limitation of this study. How can the authors rule out the possibility that their observations are not due to such a potential bias?

Abstract: MAC is not defined.

P29414,L20: “Soot” is not a synonym for BC. “Soot” includes the organic fraction.

P29415,L6: MAC is wavelength dependent. One must always report wavelength when referring to specific MAC values from the literature. Further, Bond and Bergstrom more specifically report that at 550 nm the MAC for uncoated (fresh) BC is 7.5 +/- 1.2 m²/g, not 4-8 m²/g.

P29415,L23: Since the presentation of Liu et al. (2013) is not available to the public, I

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do not believe that it is appropriate to cite here.

Measurements: The authors never mention the wavelength of their albedometer, which is a clear oversight. This is only made clear in the caption of Fig. 7.

P29418,L15: I should hope that the SP2 indicated diameters agreed well with the electrostatic selection diameters, since the SP2 is actually calibrated against size-selected particles.

SP2 calibration: There is no statement of calibration of the scattering detector. Was this not calibrated?

P29419,L12: The increase in scatter/incandescence peak ratio is only consistent with the BC particles being internally mixed with other material. It does not indicate one way or the other whether the particles are “coated” (and where I interpret “coated” to mean that the BC is surrounded by the non-BC material).

SP2 lag time: Can the authors provide any guidance as to what approximate coating “thickness” would be required to give a lagtime > 1 microsecond? In other words, can they be more specific as to what “coating” means?

SP2 size distributions and Fig. 4: The authors appear to be presenting BC size distributions where they have not accounted for the rapid fall off in sensitivity below ~100 nm. Thus, the visual nature of the size distributions is highly misleading. Similarly, they present the mass-weighted distributions as having a sharp fall off at 400 nm. This is an instrumental artefact and should be removed. Further, the mode of the mass-weighted size distributions is quite large on most days (close to 200 nm), which is more consistent with a biomass dominated area than an urban area like Houston. This leads me to wonder whether they have treated their data properly. Also, it is not clear whether the authors have accounted for the “missing mass” that is outside the SP2 detection window. Although only approximate (and uncertain), one practice is to fit the distributions to log normal modes to estimate the amount of “missing mass”. Without accounting

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for this, the reported MAC values will all be biased high (although they may still be so even if log normal fitting is performed).

Fig.4: There is no scale given for the color scale in panel B.

Table 1: Albedo does not have units.

Fig. 5: Does this figure include the measurements made on dried particles? It is never stated to what RH the drier dries the particles. From Fig. 6, it seems to be variable, and only about 40% or greater. If the dried measurements are not included, they should be, although they could be indicated as a different color to distinguish.

Fig. 5: Such a small mass scatter coefficient (MSC) at low RH suggests to me a relatively sizeable contribution of supermicron particles, which tend to exhibit smaller MSCs than do smaller particles. Do the authors have any idea what the supermicron contribution was?

P29420, L19: Technically, it is the MAC of refractory black carbon that is being reported (since this is what the SP2 measures) and not the “soot MAC”.

Fig. 7: The reported MAC at 532 nm at low RH is only 3.8-4.4 m² g⁻¹. This is much lower than one would expect for BC particles (e.g. Bond and Bergstrom, 2006). This is especially true given that it does not seem that the authors accounted for “missing mass” in their SP2 analysis, which, if accounted for, would further depress the MAC. No explanation is given.

Fig. 6 and P29421,L6: The authors report their time series in terms of seconds past a certain date. This is very difficult to follow. They should use more conventional reporting metrics, such as time of day. Given the current reporting, it is nearly impossible for the reader to figure out where the “morning hours” are, despite the bar indicating “night” and “day”.

The authors report that their BC mode diameter is 120 nm (in number space). This corresponds approximately to 200 nm in mass space. Let’s assume a coating thickness

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of 100 nm, which gives a 400 nm diameter particle. At 90% RH the GF is ~ 1.9 based on Fig. 2. This would correspond to a wet particle diameter of 760 nm. Thus, much of the space considered in Fig. 8a seems out of range for what is likely.

More on Fig. 8: In their calculations, the authors find a MAC for their uncoated particles of ~ 7 m²/g. This is around a factor of 2 larger than their observations. On top of this 7 m²/g, they find that a water coating could increase the MAC to ~ 15 m²/g (for 120 nm particles), corresponding to around a factor of 2 increase in absorption. In their observations they observed an increase from ~ 4 m²/g for “dry” particles to 15 m²/g for “wet” particles when the fraction of coated particles is large. This is a factor of 3.75, much larger than the theoretical calculations can support. This is exacerbated if one considers that only a fraction of the particles is considered “coated”. The authors mislead on P29424 by comparing absolute values of the MAC between observations and calculations, since there is not consistency with the dry particles. In other words, given that the observed dry MAC is 4 m²/g and the calculated dry MAC is 7 m²/g, one cannot directly compare an observed 15 m²/g with a calculated 15 m²/g. .this is like comparing apples and oranges.

Fig. S4 and Fig. 7: The authors bury the uncertainty in their measurements in the supplementary material. It is clear that the uncertainty at large MAC is large. .in fact about as large as the measurements themselves! It is also not clear at all how the uncertainty was actually propagated (P29422, L15).

P29421,L25: It seems clear to me that the authors cannot assess an increase from 3.8 to 4.4 m²/g for the MAC with coating fraction given the uncertainties in their measurements and the fact that “missing mass” has not been accounted for. Shifts in the BC size distribution can lead to biases in the reported MAC if there are differing amounts of “missing mass.”

Is there any correlation between the increase in MSC with RH and the increase in MAC with RH? Is the increase in MSC with RH lower when the coated fraction is lower?

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P29422,L9: I do not see how an increase in absorption of a factor of 3-4 (reported here) is consistent with laboratory measurements of BC mixed with sulfate of only 1.1 \pm 0.07, as reported in Wei et al. (2013). This is highly misleading, as written.

P29422,L15: The uncertainty propagation was performed assuming an absorption of 2 Mm⁻¹. This is almost as large as the mean value in this study (2.9 Mm⁻¹). The authors in previous lines state: “The highest measurements of MAC observed corresponded to time periods in which the concentration of BC and babs was low, and RH was high.” If this is the case, the uncertainty propagation would be more relevant using an absorption coefficient (and associated BC concentration) equal to the lower quartile value, which is only 0.62 Mm⁻¹. This would have the practical effect of increasing all the uncertainties.

Fig. 2a: How did the authors decide to use a GF most similar to ammonium sulfate (but without deliquescence)? What about the influence of organics, which would decrease the GF for a particle of a given dry size. Presumably the particle composition was not constant throughout the entire study. And it was stated that the winds were often from the south. What about the influence of sea salt, which would have a larger GF compared to ammonium sulfate? Without composition data the authors are only guessing at a value to use, and thus their truncation correction has considerable uncertainty.

References:

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